In fact, the $(fT_{1p})^{-1} \ll (fT_{2p})^{-1}$ condition (only dipolar contribution to T_1 and only scalar contribution to T_2) holds only for ^{13}C nuclear relaxation as far as the ligand is concerned (Table I). On these bases a comparative analysis of ^{13}C nuclear relaxation rates[3] is more suitable in demonstrating the N(7) involvement in metal binding. Moreover, the selective broadening of the C(5), C(8), and C(4) peaks of ATP, due to purely scalar contribution, points out the direct metal–N(7) bond.[13] These findings are further supported by recent pulsed EPR results.[19]

As conclusive remarks, combined EPR and NMR analysis is very important whenever the binding of large molecules is investigated. Since the manganous ion is widely used as a relaxation paramagnetic probe in biological systems, the following findings must be emphasized: (i) the relevance of outer-sphere species; (ii) the theoretical model for electron spin relaxation which points out the rotational mechanism with its own temperature dependence; and (iii) the existence of several τ_s values which may differ from each other by orders of magnitude, leading to more complicated nuclear relaxation behavior and to a competition with τ_r.

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References and Notes

(1) R. Phillips, *Chem. Rev.*, **66**, 501 (1966).
(2) R. M. Izatt, J. J. Christensen, and J. H. Rytting, *Chem. Rev.*, **71**, 439 (1971).
(3) Y. F. Lam, G. P. P. Kuntz, and G. Kotowycz, *J. Am. Chem. Soc.*, **96**, 1834 (1974), and references therein.
(4) V. Wee, I. Feldman, P. Rose, and S. Grass, *J. Am. Chem. Soc.*, **96**, 103 (1974), and references therein.
(5) G. P. P. Kuntz, Y. F. Lam, and G. Kotowycz, *Can. J. Chem.*, **53**, 926 (1975), and references therein.
(6) F. F. Brown, I. D. Campbell, R. Henson, C. W. J. Hirst, and R. E. Richards, *Eur. J. Biochem.*, **38**, 54 (1973).
(7) R. A. Dwek, "Nuclear Magnetic Resonance in Biochemistry", Clarendon Press, 1973.
(8) H. Sternlicht, R. G. Shulman, and E. W. Anderson, *J. Chem. Phys.*, **43**, 3125 (1965).
(9) H. Sternlicht, R. G. Shulman, and E. W. Anderson, *J. Chem. Phys.*, **43**, 3313 (1965).
(10) G. G. Hammes and D. L. Miller, *J. Chem. Phys.*, **46**, 1533 (1967).
(11) G. H. Reed, J. S. Leigh, and I. E. Pearson, *J. Chem. Phys.*, **55**, 3311 (1971).
(12) L. Burlamacchi, G. Martini, and E. Tiezzi, *Chem. Phys. Lett.*, **23**, 294 (1973).
(13) R. Basosi, F. Laschi, E. Tiezzi, and G. Valensin, *J. Chem. Soc., Faraday Trans. 1*, **72**, 1505 (1976).
(14) M. Romanelli and L. Burlamacchi, *Mol. Phys.*, **31**, 115 (1976).
(15) L. Burlamacchi, G. Martini, M. F. Ottaviani, and M. Romanelli, *Adv. Mol. Relaxation Interact. Processes*, **12**, 145 (1978).
(16) L. Burlamacchi and E. Tiezzi, *J. Phys. Chem.*, **73**, 1588 (1969).
(17) L. Burlamacchi, G. Martini, and E. Tiezzi, *J. Phys. Chem.*, **74**, 1809 (1970).
(18) W. G. Espersen and R. Bruce Martin, *J. Phys. Chem.*, **80**, 116 (1976).
(19) J. Peisach and W. B. Mims, *Int. Symp. Magn. Reson., 6th*, 146 (1977).

Covalently Attached Organic Monolayers on Semiconductor Surfaces[1]

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Abstract: Treatment of silicon or gallium arsenide with the refluxing vapors of 3-aminopropyltriethoxysilane in toluene or xylene solution results in a strictly monolayer coverage of the surface with aminopropylsilyl groups. Electron microscopy indicates that these conditions avoid the formation of polymeric globules whose presence is characteristic when the substrate is immersed in the treating solution. Ellipsometric measurement of the thickness change upon reversible adsorption of dodecyl sulfate anions indicates a closely packed layer of extended hydrocarbon chains. This implies that the coverage of the semiconductor surface with the underlying aminopropyl groups is essentially complete. Neither the rate of the silane attachment reaction nor the rate of hydrolysis is strongly affected by the doping level of the semiconductor. Reactions of the amino groups allow bonding of a variety of organic molecules to the surface. Particularly facile are (a) carbodiimide coupling of carboxylic acids, (b) conversion of the surface to a strongly acidic one, and (c) conversion of surface amino groups to isothiocyanate followed by coupling to primary amines.

Reactions of organosilanes with hydroxyl-bearing surfaces have found use in several diverse areas. Linking of molecules of biochemical interest to porous glass, for the purposes of affinity chromatography and enzyme immobilization, have received a great deal of attention.[2-4] The oldest and most widespread use is in promoting the adhesion of polymers to fiberglass.[5-7] More recent interest has centered on electrode modifications,[8-9] catalysis,[10,11] and adhesion promotion in electronic microcircuit processing.[12]

We have investigated some monolayer reactions of organosilanes on surfaces of elemental silicon. One motivation for this was to provide methods for the preparation of chemical systems that can yield information about the interaction between electronic levels of various attached organic moieties and the electronic bands of the semiconductor. Desirable organic moieties would be those that have strong acceptor or donor properties, or carry a permanent ionic charge. Such an interaction, at least in principle, could lead to utilization in solar cells and other semiconductor devices. The reaction of organosilanes on elemental silicon substrates, however, also provides an important and convenient model system for most of the diversely used silanation reactions referred to above. As is well known,[13] freshly etched silicon exposed to air at room temperature is rapidly covered by a thin, coherent oxide layer whose logarithmic rate of growth ensures that in the experimentally accesible time period (1 min to 1 year) the thickness remains in a convenient range (0.5 to 2.5 nm). One expects that the chemical properties of this oxide are not grossly different from bulk silica while it is thin enough to permit tunneling of electrons and thus avoid charging up of the surface in electron microscopy or spectroscopies. The model system is thus free from the disadvantage inherent in fibrous and porous silica or glass substrates whose insulating nature interferes with the utilization of some of the more sophisticated surface analytical techniques. Furthermore, the reflectivity of the underlying silicon substrate allows the use of ellipsometry for the precise

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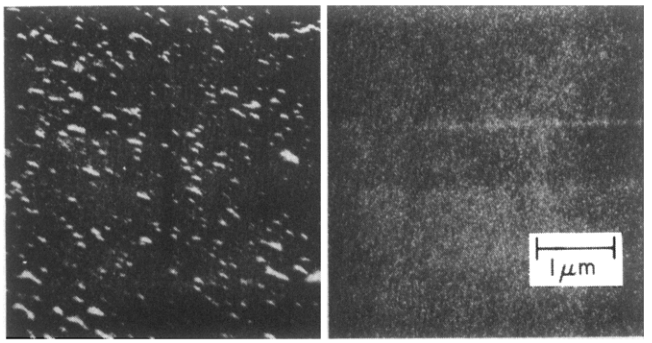
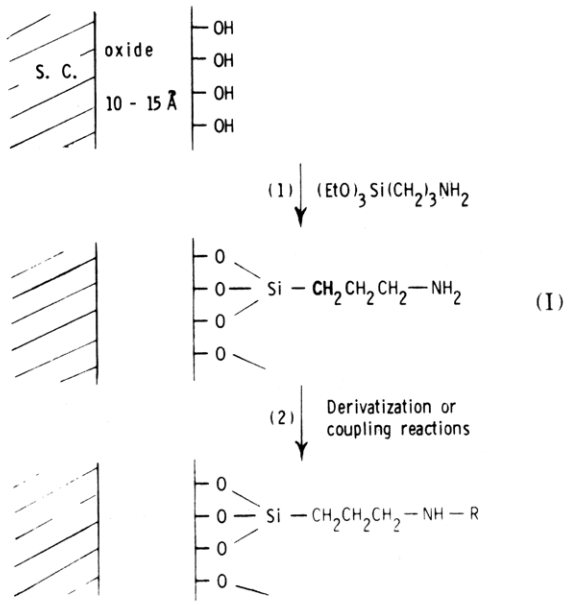


Figure 1. Scanning electron micrographs of silicon surfaces: (a) treated with a dry toluene solution of **1** and (b) untreated or silanation performed in the vapor phase.

Monolayer Reactions Involving **1** at a Semiconductor Surface[a]



[a] The exact number of siloxane bonds linking the organosilicon atoms to the substrate (as opposed to neighboring organosilicon atoms) is not known.

measurement of the change in thickness of the transparent layer after reactions involving the organosilane are carried out.

This paper examines the reactions illustrated in scheme I. We first describe reaction conditions which avoid attachment to the silicon substrate, of polymeric globules resulting from side reactions of the 3-aminopropyltriethoxysilane (**1**), as observed with electron microscopy. Essentially complete coverage of the surface with a monomolecular layer of closely packed aminopropyl groups is implied by the results of ellipsometric measurements of the subsequent reversible adsorption of dodecylsulfate ions. This subsequent adsorption also results in a striking change in the contact angle of water on this surface, and thus provides a rapid qualitative test for the presence of primary amino groups remaining after the surface has been exposed to reactants. We have used it to assay the stability of the aminopropylsilanated (henceforth abbreviated as APS) surface, and to examine derivatization and coupling reactions of the surface amino groups.

Reaction of Aminopropyltriethoxysilane with Silicon

Silicon wafers were initially treated, as recommended in the literature[2,8,10] for silica substrates, with a refluxing solution

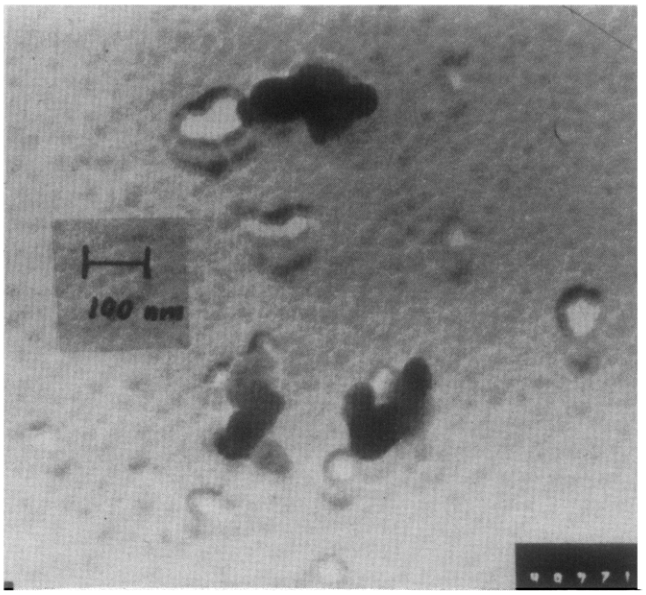


Figure 2. Transmission electron micrograph of adherent particles found in the solution phase silanation process.

of 5% **1** in toluene for 16 h. The formation of a heavy haze on the surface was observed. Fractionation of the aminopropyltriethoxysilane, careful drying of the solvents and glassware, and working under nitrogen atmosphere reduced the extent of haze formation, but light scattering was still clearly observable on the reflective substrate under oblique illumination. The scattering centers were found to be too small to be resolved by optical microscopy.

Figure 1a shows a scanning electron micrograph of an APS silicon prepared under dry conditions. Comparison to a clean, untreated Si surface, shown in Figure 1b, indicates the presence of particles of typical dimensions of about 100 nm. Transmission electron micrographs, such as seen in Figure 2, indicate that the individual particles are of irregular shape and have no sharp edges. Selected area electron diffraction confirms that the particles are amorphous. We identify them as polymer globules. Their source, presumably, is the well-known polycondensation reaction of alkoxysilanes.

In order to eliminate the formation of adherent polymer globules, we found it necessary to carry out the surface reaction in the apparatus shown in Figure 3. The wafers to be treated are held in a quartz rack and are in contact only with the condensing vapors of the refluxing mixture. Under these conditions the vapor pressure of **1** is sufficient (ca. 64 and 19 torr in the pure state at the boiling points of xylene and toluene, respectively) to be transported to and to react at the surface. Dimeric and oligomeric precursors, however, due to their lower vapor pressure remain preferentially in the bottom reservoir. Scanning electron micrographs of silicon wafers treated this way are in fact indistinguishable from the bare substrates, indicating the absence of any particles larger than about 10 nm.

The presence of a monolayer of covalently bound aminopropyl groups is best demonstrated by subsequent adsorption and ellipsometric techniques.

If one immerses an amino group covered substrate in a saturated solution of sodium dodecyl sulfate (NaDS), in contrast to a bare (oxide coated) substrate, DS ions are reversibly adsorbed. They can be removed under conditions where covalent bonds are not attacked. The cycling of adsorption and desorption was followed by ellipsometry. The results are summarized, along with other relevant data in Table I.

Ellipsometry, in principle, is capable of simultaneously de-

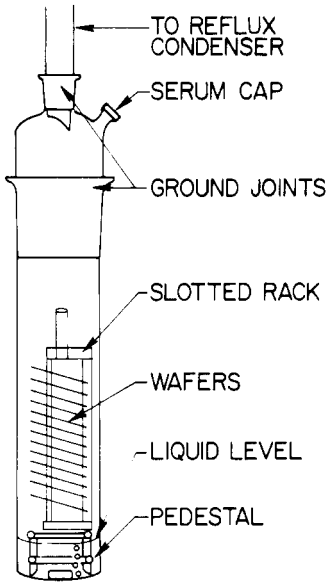


Figure 3. Apparatus for vapor phase silanation of silicon wafers.

termining the thickness and the refractive index of a thin film covering a reflective substrate. With films thicknesses in the few angstroms range, however, the measured ellipsometric parameters are very insensitive to changes in the refractive index,[14,15] and it is advisable to compute film thickness using an independently determined or assumed value of the index. Since the difference in refractive indices between the native oxide on silicon (n = 1.462)[14] and that of model compounds such as dodecanoic acid (n = 1.430), hexaethyldisiloxane (n = 1.434), and 1,5-diaminopentane (n = 1.456)[16] resembling the attached organic moieties is small, the computations were carried out assuming a single, homogeneous, nonabsorbing film, with n = 1.462. Using different values for n within the range of the model compounds cited results in a change of the computed thicknesses of less than 2.5%. Since the precision of ellipsometric thickness measurement is much better than its absolute accuracy, all data shown are referenced to a freshly (1 to 2 h) HF etched silicon sample; its oxide thickness is assumed to be 1.0 nm.[13]

The most significant result shown in Table I is the observation of a reversible 1.6-nm change in the transparent layer thickness between immersions of a properly aminopropylsilanated substrate in NaDS solution and glacial acetic acid, respectively. This distance agrees very well with the difference in the lengths of *extended chain* dodecyl sulfate (1.9 nm) and acetate (0.38 nm) ions. Since ellipsometry averages over the surface, we conclude that within the precision of the measurement, the surface coverage with extended DS chains is complete. This result implies that the surface density of amino groups also corresponds to that of closely packed hydrocarbon chains, that is 5×10^{14} cm^{-2}.

Other ellipsometric results of Table I indicate that there is a growth in the oxide thickness under the reaction conditions used for silanation (even in the absence of **1**), of about 1.1 nm. The excess thickness of about 0.8 nm of the acetic acid stripped sample over the blank is consistent with an organic layer of covalently bound closely packed aminopropylsilyl groups in the acetate form.

To obtain the complete coverage in the silanation procedure, it was found necessary to pretreat the cleaned Si wafers in nitric acid as described in the Experimental Section. It is assumed that in the absence of this procedure the low surface concentration of silanol groups on the substrate limits the extent of the reaction. The nitric acid treatment, however, is also the main contributor to the increase in oxide thickness that is seen in the "blank" sample in Table I. While substantially shorter HNO_3 treatment reduced the aminopropyl coverage, longer HNO_3 treatment resulted in further increase only in oxide thickness but not in the thickness of the reversibly adsorbed dodecyl sulfate.

Table I. Ellipsometricly Measured Transparent Layer Thickness (Including Oxide), t, of an Aminopropylsilanated Silicon Surface and Its Change in Dodecyl Sulfate Adsorption-Desorption Cycles (Water Contact Angles α, are also Shown)

surface	t, nm	α, deg
HF etched, 0.5 h air	1.0	80
blank: HNO_3, toluene vapor	2.1	52
APS, DS adsorbed	4.5	93
CH_3COOH stripped	2.9	45
DS readsorbed	4.4	90
restripped	2.7	44

The last column of Table I shows the contact angle of water measured on the variously treated surfaces. On APS silicon with dodecyl sulfate adsorbed it is over 90°. Contact angles this high are generally seen only on nonpolar, low-energy surfaces, such as fluorocarbons or hydrocarbons, thus confirming the presence of a coherent layer of adsorbed DS ions. In the stripped form, as well as in the absence of aminopropyl surface groups, the contact angle is, as expected, much lower. While low water contact angles are not specific to any particular surface species, they are diagnostic of the absence of a coherent coverage with hydrocarbon chains, and can thus be utilized to study the stability and reactions of APS surfaces.

Stability of the APS Surface

Since the high water contact angle is diagnostic of the presence of a coherent layer of hydrocarbon chains on the surface, we have utilized these measurements for assaying the stability of the aminopropyl groups bound to the surface. They were also used for establishing conditions for coupling reactions of the surface amino groups. While occasionally the results were confirmed by more specific and more sophisticated analytical techniques, the contact angle measurements proved to be rapid and very convenient for cataloguing the effectiveness of a relatively large number of procedures.

Refluxing in dry, apolar solvents, such as toluene or CS_2, leaves the water contact angle (as measured in a subsequent test) unaltered on an APS-DS surface. In these solvents then, dodecyl sulfate is not desorbed. Similarly, no change in α, hence no decomposition, occurs upon standing in laboratory air at room temperature for over 3 months, or at 150 °C for 2 h.

Refluxing in some other liquids results in the removal of the adsorbed DS but not in the removal of the covalently bound aminopropyl groups. This is indicated by a drop in the water contact angle after the treatment and by the fact that the contact angle is restored to its original value (>90°) upon immersion in NaDS. This behavior was observed in dry, apolar solvents in the presence of base (pyridine, triethylamine, or solid Na_2CO_3). Some attack on the aminopropyl groups (i.e., incomplete restoration of water contact angle upon immersion in NaDS) is observed upon lengthy (>2 h) reflux in dry, aprotic, polar solvents (tetrahydrofuran, chloroform, or acetonitrile).

A substantial removal of APS groups was observed upon treatment with protic solvents under relatively mild conditions, for example, in ethanol in a 1-h reflux, or standing for 16 h at room temperature. Similarly, immersion in water or in aqueous solutions for times longer than a few minutes resulted in a substantial attack on the aminopropyl groups. The unrestorable decrease in contact angle was observed even if the water was

buffered at pH 7, or when dissolved oxygen was rigorously removed indicating that the loss of the APS groups was hydrolytic.

The lack of long-term hydrolytic stability of APS silicon in an aqueous environment is at variance with observations on porous glass.[3] We interpret the difference as being due to the presence of a three-dimensional network of siloxane polymer on at least part of the porous glass surface.

We have looked for, but found no significant effect of the location of the Fermi level in the bulk of the silicon substrate on the attachment or on the hydrolytic removal of APS groups. Silicon wafers of six different dopings ranging from 0.1 ohm cm p type to 0.1 ohm-cm n type were silanated overnight (as detailed in the Experimental Section), and after immersion in NaDS solution all were found to have water contact angles over 90°. Shorter (3 h) but otherwise identical treatment led to incompletely silanated samples showing no trend, however, in contact angle with doping level. The fully silanated samples were then subjected to hydrolysis by immersion in 0.5 M aqueous HCl solution at room temperature for 15 min. After readsorption of DS by immersion in NaDS solution, the water contact angles ranged from 73 to 86°, with no observable trend with doping level or type.

Reactions of the Surface Amino Groups

The APS surface exhibits most of the reactions expected of primary amino groups. Some of the coupling reactions investigated by water contact angle measurements are summarized in Table II. Thus amide formation with carboxylic acid with diimide[3c,17] coupling reagents (reaction II) proceeds smoothly to high conversion at low temperature.

$$\underset{\textbf{2}}{\Sigma\text{-}NH_2 + HOOCR} + \underset{\textbf{3}}{R'N{=}C{=}NR'} \xrightarrow{\text{pyridine}} \underset{\textbf{4}}{\Sigma\text{-}NHCOR} + R'NHCONHR' \quad \text{(II)}$$

2a, R = $C_{11}H_{23}$
b, R = $(CH_2)_4\overline{CH\,CH_2CH_2SS}$
c, R = $CH_2N(CH_2COOH)C_2H_4N(CH_2COOH)_2$
d, R = ferrocenyl
e, R = tetrathiofulvalenyl
3a,4a, R′ = cyclohexyl
3b,4b, R′ = isopropyl

Evidence for this is provided by the negligible difference in the water contact angle on the product surface as prepared (α_p) and after attempted dodecyl sulfate ion adsorption (α_{DS}), and by the high value of α_p in the case of fatty acids and its lower value with more polar R. Covalent bonding of the acids to the surface is indicated by the small change in water contact angle ($\alpha_p - \alpha_w$) upon washing in solvents expected to remove physisorbed or saltlike acid groups. Although **3a** and **3b** are equally effective in bringing about the amide formation, the diisopropyl derivative is the preferred one as with this reagent no complications arise due to an insoluble byproduct occluding the surface.

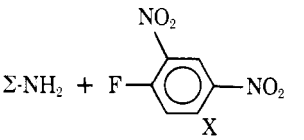
Formation of secondary amines with 2,4-dinitrofluorobenzene and 2,4-dinitro-1,5-difluorobenzene (reaction III)[18] proceeds as indicated by the drastically reduced DS adsorption compared to blank. The use of a variety of reaction conditions (solvent, base, temperature and time), however, still did not result in an assuredly high conversion without removal of some surface amino groups in the corresponding blank reaction.

Condensation reactions (reaction IV) of the surface amino groups with carbonyl compounds such as 2,4,5,7-tetranitro-9-fluorenone (**6**) or glutaraldehyde[3c] (**7**) do not take place to any significant extent, or the Schiff bases formed are excessively labile. This follows from the high α_{DS} observed indicating that the surface retains to a high degree its ability to adsorb dodecyl sulfate ions after the attempted reaction.

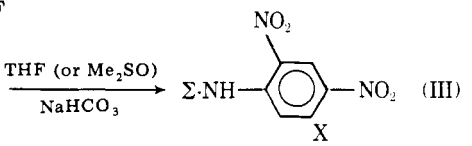
Table II. Water Contact Angles on Aminopropylsilylsilicon Surfaces Following Coupling Reactions Described in Text[a]

reaction	reagents	α_p	α_w	α_{DS}	α_{DA}
II	**2a, 3a**	91	91	93	
II blank	**2a**; no **3**	67	60	92	
II	**2a, 3b**	92	92	93	
II	**2b, 3b**	90	90	90	
II	**2c, 3b**	46	42	43	42
II	**2d, 3b**	26	21	24	
II	**2e, 3b**	58	63	62	
III[b]	**5a**	53	52	55	
III blank[b]	no **5**	51		77	
III[c]	**5a**	47		57	
III blank[c]	no **5**	36		81	
III[d]	**5b**	50		54	
IV	**6**	34		82	
IV	**7**	55		77	72
V	**8**	35		30	76
VI	**9**	36		34	79
VI blank	no **9**	36		81	36
VII	**3a, 11a**	68	60		77
VIII	**12, 11a**	82	81	85	
IX	**3a, 11a**	89	87	89	
IX blank	**11a**; no **3**	49	49	86	

[a] α_p, on surfaces as prepared; α_w, after repeated alcohol and water wash; α_{DS}, after immersion dodecyl sulfate; and α_{DA}, after immersion in decylamine solutions. [b] THF reflux, 2 hr. [c] Me_2SO, 25 °C, 64 h. [d] THF, 25 °C, 20 h.



5a, X = H
b, X = F



(III)

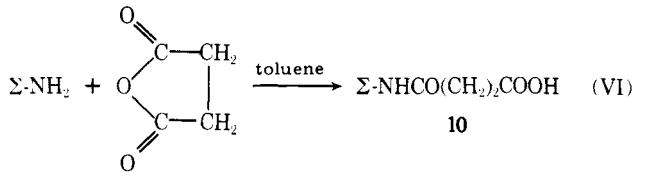
$$\Sigma\text{-}NH_2 + OCRR' \xrightarrow{-H_2O} \Sigma\text{-}N{=}CRR' \quad \text{(IV)}$$

At least two reactions are available to convert the basic APS surface into an acidic one. The formation of a disubstituted thiourea[19] in reaction V with p-sulfophenyl isothiocyanate (**8**) proceeds with ease.

$$\Sigma\text{-}NH_2 + \underset{\textbf{8}}{SCNR} \xrightarrow[\text{pyridine}]{CH_3CN} \Sigma\text{-}NHCSNHR \quad \text{(V)}$$

R = $C_6H_5SO_3H$

This is shown by the lack of adsorption of dodecyl sulfate on the treated surface and the high water contact angle observed upon decylamine adsorption (α_{DA}). Similarly, the high α_{DA} and low α_{DS} observed following reaction VI



(VI)

9 **10**

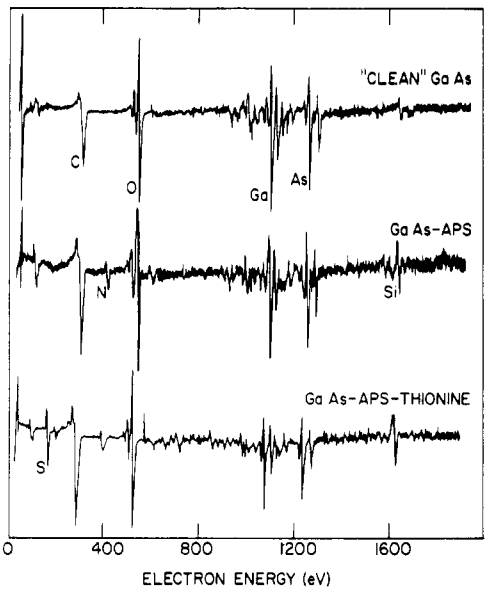


Figure 4. Auger spectra of GaAs clean, after silanation, and after isothiocyanate coupling of thionine.

in sharp contrast to the blank reaction leads to the conclusion that monoamide formation with excess succinic anhydride (**9**) is facile.

The major use of the product analogous to **10** obtained on porous glass[3c] is as an intermediate for diimide coupling with proteins through the latter's amino groups. The water contact angle of the product of the surface reaction VII would, therefore, be expected to be high, resistant to washing ($\alpha_w \approx \alpha_p$), and not to be raised by further adsorption of decylamine.

$$\underset{\textbf{11}}{\textbf{10} + H_2NR} + \textbf{3a} \rightarrow \Sigma\text{-}NHCO(CH_2)_2CONHR + \textbf{4a} \qquad \text{(VII)}$$

$$R = C_{10}H_{21}$$

As seen from Table II, however, this is not the case, and no significant improvement in the yield of this coupling reaction could be achieved by variation in the reaction conditions.

A clearly superior method of coupling primary amines is through an isothiocyanate intermediate **13.** A thiophosgene reflux (route VIII), recommended for the conversion of surface amino groups on organic substrates[20] and on porous glass,[3c] yields satisfactory results as reflected in the observed contact angles but suffers from the presence of a harsh reagent and byproduct.

$$\underset{\textbf{12}}{\Sigma\text{-}NH_2} + CSCl_2 \xrightarrow[\text{reflux}]{CHCl_3} \underset{\textbf{13}}{\Sigma\text{-}NCS} + 2HCl$$

$$\xrightarrow[\text{in pyr}]{H_2NR} \Sigma\text{-}NHCSNHR \qquad \text{(VIII)}$$

$$\underset{}{\Sigma\text{-}NH_2} + CS_2 + \underset{\textbf{3a}}{R'N{=}C{=}NR'} \xrightarrow[\text{low } T]{\text{pyr}} \underset{\textbf{13}}{\Sigma\text{-}NCS}$$

$$\xrightarrow[\text{in pyr}]{H_2NR} \Sigma\text{-}NHCSNHR \qquad \text{(IX)}$$

The most convenient route utilizes the condensation of the surface amino groups with CS_2 in the presence of diimides (route IX) which was adapted from Jochims' synthesis[21] for soluble isothiocyanates. When followed by reaction with decylamine, this route to intermediate **13** also gives the highest and most stable water contact angles indicative of high coverage of the surface with covalently bound hydrocarbon chains.

Confirming evidence for some of the above surface reactions is provided by Auger spectroscopy. Figure 4 illustrates the change in the elements present at the surface of a GaAs substrate in a sequence of reactions. The top trace indicates the presence of oxygen and carbon, in addition to Ga and As, in the surface layer of the "clean" substrate. After treatment with aminopropyltriethoxysilane (middle trace) peaks indicating the presence of silicon (1611 and 83 eV) and nitrogen (381 eV) appear. Finally, the lowest trace shows the incorporation of sulfur (150 eV) in the surface layer in reaction VIII followed by coupling with 3,7-diaminophenothiazinium chloride (thionine).

Experimental Section

Substrates. Silicon wafers, 25.4-mm diameter, 0.25-mm thick, one surface polished to better than 0.3 μm, were supplied by Rockwell International. They were Czochralski grown, had ⟨111⟩ orientation, and were phosphorus or boron doped to 0.1, 1, or 10 ohm cm resistivity. Prior to use, they were cleaned by immersion for 15 s each in a series of ultrasonically agitated solvents (acetone, toluene, acetone, EtOH, H_2O) then for 60 s in ultrasonically agitated 2% Alkonox solution, rinsed in H_2O and EtOH, and dried with streaming vapors of boiling trichloroethylene. They were etched for 15 s in stirred hydrofluoric acid and rinsed in H_2O. Wafers showing noticeable light scattering at this stage under oblique illumination with a 100 W focused microscope lamp were discarded.

Gallium arsenide crystals (Laser Diode Laboratories, Inc.) were cleaned in a series of solvents (acetone, trichloroethylene, ethanol) then anodized[22] at 50 V in pH 2 phosphoric acid. The approximately 90-nm oxide layer was removed prior to use by dipping in HCl.

Nitric Acid Treatment. The cleaned and etched silicon wafers were placed in a rack and immersed in concentrated HNO_3 at room temperature for 2 h. After several H_2O rinses the wafers remained wetted by water. The minimum time of HNO_3 immersion to make the wafers hydrophilic varied from batch to batch from 15 to 90 min.

Solvents. Toluene and xylene for silanation were dried by distillation from CaH_2 under nitrogen. Pyridine was stirred consecutively with KOH, alumina, and molecular sieves, filtered, and fractionated. $CHCl_3$ was freed from EtOH by five H_2O washed and dried with silica gel and Drierite. Other solvents, when appropriate, were dried with molecular sieves or Drierite. All chemicals were stored and solutions made up in a glove-bag under dry N_2 atmosphere.

Aminopropylsilanation. 1 (PCR, Inc.) was distilled twice in vacuo (bp 121 °C at 26 torr). The clean substrates were loaded face down in the rack in the apparatus shown in Figure 3. The apparatus containing the substrates was dried by evacuating with a rotary pump (ground joints sealed with Teflon sleeves) while heating the section below the ground joint with heater tape to 120°-140 °C for 0.5 h. The apparatus was then back filled with dry N_2, and it was surrounded by a N_2 purged shroud after removal of the pump and heater tape. A solution of 1 mL of **1** in 13 mL of toluene or xylene was injected through the serum cap and was refluxed for 16 h at a heating rate that assured that the condensible vapors extended at least 30 mm above the top wafer. The apparatus was dismantled and the wafers were rinsed in toluene inside a glove bag. The wafers were further rinsed in EtOH and H_2O in room air, and unless immediately used were stored after DS adsorption.

Liquid phase APS treatment, which was found to result in some polymer deposition on the substrate, was carried out under the same conditions except that a low wafer rack and a solution of 2 mL of **1** in 40 mL of toluene were used. Omission of the N_2 shroud and relaxation of the apparatus drying caused no noticeable change in the vapor phase treated samples, but increased the haze on liquid phase treated wafers.

Dodecyl Sulfate Adsorption and Desorption. NaDS (1 g) was shaken with 200 mL of H_2O and the formed liquid crystalline phase was allowed to settle. The clear, saturated aqueous phase, 0.5 mL, was allowed to stay in contact with individually held wafers for 1 min. The wafers were rinsed with the minimum amount (i.e., 3 × 0.3 mL) of H_2O required for the removal of excess adsorbate. The rinse water

rolls off without a trace from surfaces on which DS adsorbs; from others it was blown off with N_2.

Adsorbed DS was replaced by acetate by a 60-s immersion in glacial acetic acid, EtOH rinse, and drying in the vapors of boiling C_2HCl_3. It was completely desorbed by a 15-s immersion in hot (~100 °C) pyridine. The first of these treatments resulted in a partially water wettable surface which became completely hydrophilic after a 1-min wash in H_2O; the pyridine-treated surface was hydrophilic. Both could be made hydrophobic again by immersion in NaDS.

Reaction with Carboxylic Acids. APS silicon wafers in their DS form were immersed into solutions or suspensions of 0.20 mmol of the acids **2** in 2.4 mL of dry pyridine and placed in a freezer. After stirring in 0.25 mmole of liquid diimide, the temperature was raised in four steps to 50 °C over a 3 h period, in the middle of which 0.02 g of *N*-hydroxysuccinimide[23] was added. The wafers were rinsed in pyridine and EtOH, then dipped into boiling pyridine to remove the adhering byproduct **4a**, and rinsed in EtOH and H_2O.

Reaction with (Di)fluorodinitrobenzene. APS wafers were refluxed in the solution of 0.2 mL of **5** in 20 mL of THF in the presence of 0.6 g of $NaHCO_3$ for 15, 60, 120, and 220 min, or allowed to stand at room temperature for 16 h. With **5a**, best results were obtained (see Table II) with 120-min reflux. No improvement was seen by adding 0.1 mL of pyridine catalyst or using Me_2SO as solvent. With **5b** better results were obtained by allowing the solution to stand for 16 h at 20 °C (Table II) than refluxing.

Attempted Reaction with Carbonyl Compounds. An APS silicon wafer was refluxed for 1 h in a solution of 0.10 g of **6** in 20 mL of dry toluene and then rinsed in toluene, EtOH, and H_2O. Another wafer was treated for 15 min in a solution of 0.5 g of **7** in 20 mL of 0.1 M aqueous phosphate buffer solution (pH 7.0).

Reaction with Isothiocyanates. An APS silicon wafer was refluxed in a mixture of 40 mL of acetonitrile, 0.2 mL of pyridine, and 0.96 g of the Na salt monohydrate of **8** (Aldrich) for 30 min and rinsed in hot acetonitrile and EtOH.

Reaction VI with Succinic Anhydride and Attempted Amide Coupling (VII). APS wafers were refluxed in a solution of 1.0 g of **9** in 20 mL of dry toluene in the presence of 0.5 mL of pyridine and rinsed in toluene, EtOH, and H_2O. Adsorption and contact angle tests indicated acidic surface. A product wafer was immersed in a solution of 0.05 g of **11a** and 0.10 g of **3a** in 5 mL of dry ether for 16 h at 20 °C. Other attempts for amide coupling included using toluene solvent, using THF solvent and reflux, and acidifying the ether solution to about pH 3 with HCl.

Surface NCS with Thiophosgene. APS silicon wafers were refluxed for 4 h in a solution of 5 mL of freshly distilled **12** in 50 mL of dry $CHCl_3$. They were rinsed in $CHCl_3$ and toluene.

Surface NCS with CS_2 + Diimide. To APS silicon wafers placed in 30-mL weighing dishes were added 1-mL aliquots of a solution of 1.3 g of **3a** in 5 mL of CS_2 and 5 mL of pyridine. They were allowed to stand 16 h at 20 °C in a glove bag and then were rinsed in pyridine and THF.

Coupling of Surface NCS to Amines. Wafers freshly prepared by either of the above two methods were immersed in a solution of 0.1 g of **11a** in 2 mL of THF. After 30 min 0.03 mL of Et_3N was added and allowed to stand for a further 0.5 h. The wafers were rinsed in THF, EtOH, and H_2O. Similar results were obtained using EtOH as solvent which allowed coupling to primary amines insoluble in THF.

Contact angle measurements were performed with a Rame-Hart Inc. Model A-100 telescope goniometer. All numbers listed are advancing contact angles of 1-μL H_2O drops, averaged over three drops at various locations on the surface. The washing procedure referred to in Table II to remove absorbed but not covalently bonded alkyl derivatives consisted of a 60-s immersion in CH_3COOH followed by EtOH and H_2O rinses, or 3 min under running deionized H_2O interrupted by three EtOH rinses.

Ellipsometry. An automated ellipsometer, described in detail by Hauge and Dill,[15] was used in the "thin film mode".

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References and Notes

(1) Presented in part at the 174th National Meeting of the American Chemical Society, Chicago, Ill., Aug. 1977, Abstract COLL-12.
(2) C. R. Lowe and P. D. G. Dean, "Affinity Chromatography", Wiley, New York, N.Y., 1974.
(3) (a) H. H. Weetall, *Nature (London)*, **223**, 959 (1969); (b) H. H. Weetall and A. M. Filbert in "Methods of Enzymology", Vol. 34, Academic Press, New York, N.Y., 1974, pp 59–72; (c) H. H. Weetall, *ibid.*, Vol. 44, 1976, pp 134–148.
(4) P. J. Robinson, P. Dunnill, and M. D. Lilly, *Biochim. Biophys. Acta*, **242**, 659 (1971).
(5) E. P.Plueddeman, *SPI Annu. Tech. Symp., Proc., 24th*, Section 19-A, 1 (1969).
(6) W. D. Bascom, *J. Colloid Interface Sci.*, **27**, 789 (1968).
(7) N. L. Jarvis and W. A. Zisman, *Bull. Soc. Chim. Fr.*, 3203 (1970).
(8) (a) P. R. Moses, L. Wier, and R. W. Murray, *Anal. Chem.*, **47**, 1882 (1975); (b) P. R. Moses and R. W. Murray, *J. Am. Chem. Soc.*, **98**, 7435 (1976)
(9) B. E. Firth and L. L. Miller, *J. Am. Chem. Soc.*, **98**, 8273 (1976).
(10) O. Leal, D. L. Anderson, R. G. Bowman, F. Basolo, and R. L. Burwell, Jr., *J. Am. Chem. Soc.*, **97**, 5125 (1975).
(11) K. G. Allum, R. D. Hancock, I. V. Howell, S. McKenzie, R. C. Pitkethly, and P. J. Robinson, *J. Organomet. Chem.*, **87**, 203 (1975).
(12) K. L. Mittal and D. F. O'Kane, *J. Adhes.*, **8**, 93 (1976).
(13) S. I. Raider, R. Flitsch, and M. J. Palmer, *J. Electrochem. Soc.*, **122**, 413 (1975).
(14) R. J. Archer, *J. Electrochem. Soc.*, **104**, 619 (1957).
(15) P. S. Hauge and F. H. Dill, *IBM J. Res. Dev.*, **17**, 472 (1973).
(16) R. C. Weast, Ed., "Handbook of Chemistry and Physics", 55th ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1974.
(17) J. Rebek and D. Feitler, *J. Am. Chem. Soc.*, **95**, 4052 (1973).
(18) H. Zahn and J. Meierhofer, *Makromol. Chem.*, **26**, 153 (1958).
(19) J. K. Inman, J. E. Hannon, and E. Appella, *Biochim. Biophys. Res. Commun.*, **46**, 2075 (1975).
(20) (a) R. Axen and J. Porath, *Acta Chem. Scand.*, **18**, 2193 (1964); (b) *Nature (London)*, **210**, 367 (1966).
(21) (a) J. C. Jochims and A. Seeliger, *Angew. Chem., Int. Ed. Engl.*, **6**, 174 (1967); (b) J. C. Jochims, *Chem. Ber.*, **101**, 174 (1968).
(22) B. Schwartz, *Crit. Rev. Solid State Sci.*, **7**, 609 (1975).
(23) N. Izumiya and M. Muraoka, *J. Am. Chem. Soc.*, **91**, 2391 (1969).